Abstract No. naya317

Alloy-Induced Enhancement of Coster-Kronig Decay in the Dilute Pd/Ag(100) Surface Alloy

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Beamline: U16B

Introduction: Surface alloys are a class of bimetallic systems where the two metals intermix only in the first atomic layer. Some surface alloys occur between immiscible metals while others are in a kinetically limited metastable state. Typically, surface alloys occur at very low impurity concentrations (< 10% ML) and their electronic structure differs significantly from that of their parent materials. Auger-photoelectron coincidence spectroscopy (APECS) is ideally suited for studying the electronic properties of these systems, as it is very surface sensitive, it is element specific, and the background from the host materials can be eliminated.

Methods and Materials: Using APECS, we have measured the line shape of the Pd M_4VV and M_5VV Auger transitions in coincidence with Pd $3d_{3/2}$ and $3d_{5/2}$ core photoelectrons, respectively, from the Pd/Ag(100) surface alloy system. The surface alloy was prepared *in-situ* by evaporating ~ 0.2 ML of Pd on an atomically clean, well-ordered Ag(100) surface. Two electron energy analyzers were used to perform the measurements. One remained fixed on the core level of interest while the other scanned energy region of the Pd Auger transitions.

Results: The Pd $M_{45}VV$ Auger transition is known to have an anomalous line shape in bulk Pd/Ag alloys when the Pd concentration is 10% or less. Fig. 1 below shows singles Pd $M_{45}VV$ Auger spectra (thin solid curves) obtained from 0.2 ML Pd on the Ag(100) surface. Features at 325 eV and 330 eV constitute the anomalous aspects of this line shape, as they are absent from either atomic or elemental metallic Pd Auger spectra. However, this surface alloy spectrum is essentially identical to that found for dilute bulk Pd/Ag alloys [1]. As we have shown previously, these features are associated with a virtual bound state at the Pd sites, as demonstrated by the dashed curves in each panel [2,3]. It is clear, however, that there is considerable excess emission between 325 eV and 320 eV in the coincidence M_4VV spectrum that is not accounted for by the theory. The energy distribution of this excess emission is consistent with a Coster-Kronig (CK) decay of the Pd $3d_{3/2}$ level where the core hole first migrates to the $3d_{5/2}$ level before undergoing a core-valence-valence decay. These data indicate (see figure below) that as much as 50% of the emission is associated with this CK decay path. This is in sharp contrast to metallic Pd where at most 10% of the M_4VV spectral weight is associated with the CK channel. We posit that the enhanced CK transition rate is the result of alloy-induced modifications of the local electronic structure at the Pd site.

Conclusions: APECS measurements have revealed an anomalously large Coster-Kronig decay channel in the dilute Pd/Ag(100) surface alloy system. These results indicate that modification of the local electronic structure in surface alloy systems can dramatically affect the photoexcitation/decay process.

Acknowledgments: This work was supported by the NSF under grants NSF-DMR98-01681 and NSF-DMR-98-12628, by the Petroleum Research Fund under grant ACS-PRF-33750-AC6,5 and the Division of Material Sciences U. S. Department of Energy under Contract No. DE-AC02-98CH10886.

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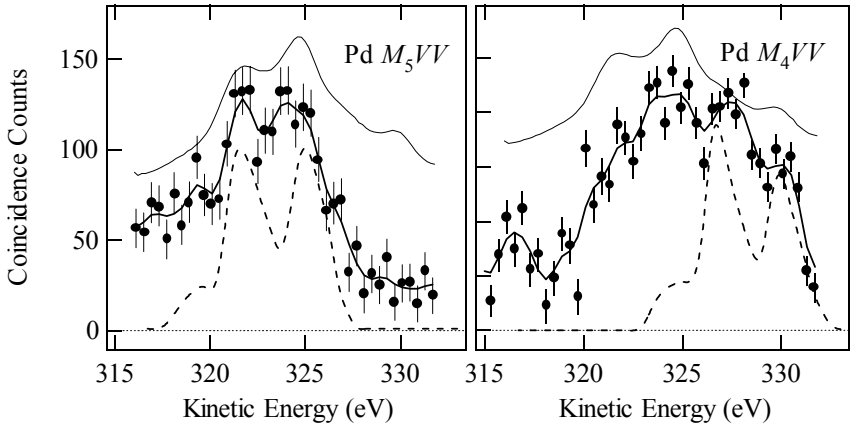

Fig. 1: Coincidence Pd M_5VV and M_4VV Auger spectra from the 0.2 ML Pd/Ag(100) system.